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ZnO/Cu(InGa)Se₂ Solar Cells Prepared by Vapor Phase Zn Doping

Contractual Origin of the Invention

5   The United States Government has rights in this invention under Contract No. DE-AC3699GO10093 between the United States Department of Energy and the National Renewable Energy Laboratory, a division of the Midwest Research Institute.

Technical Field

The present invention relates to Zinc oxide/ Copper Indium Gallium Selenium

10   Disulfide solar cells characterized by conversion efficiencies of >11%. The cells are prepared by subjecting Copper Indium Gallium Disulfide (CuInGaSe₂) or CIGS thin films to evaporant species from zinc acetate dihydrate at varying substrate temperatures, and sputter depositing ZnO thereon to provide a transparent electrode for the cell. The innovation of the invention constitutes a basis for in-line junction

15   fabrication processes for preparing CIGS thin films that do not require the use of a Cd compound and requires no buffer layers.

Background Art

Processes for manufacture of high light to electrical energy conversion efficiency thin film photovoltaic cells are known to utilize a first layer of copper

20   indium diselenide in heterojunction with one or more layers of cadmium sulfide.

For example, U.S. Pat. No. 4,335,266 discloses a method for forming a copper indium diselenide layer in two distinct regions, wherein the first region contains an excess of copper and the second region is copper deficient. Diffusion between the two layers achieves a uniform copper indium diselenide structure to reduce the formation

25   of pure copper nodules near the copper indium diselenide surface where the cadmium sulfide layer is to be deposited. However, despite the improvements in the copper indium diselenide layer, it has still been found necessary to deposit a cadmium sulfide layer to achieve high efficiency.

While various improvements have been made in the manufacture of copper

30   indium diselenide CdS cells, several complications remain. For example, chemical

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bath deposition of cadmium sulfide is used to produce the highest efficiency devices.
However, this step involves a slow wet chemical step inconsistent with an otherwise
in-line dry fabrication process. Moreover, cadmium and thiourea are highly toxic
materials which escalate manufacturing costs as a result of the handling and disposal
5   of these hazardous waste materials.

Several attempts to avoid handling complications inherent in the use of CdS
are disclosed in "A ZnO/p-CuInSe$_2$ Thin Film Solar Cell Prepared Entirely by Spray
Pyrolysis," M. S. Tomar and F. J. Garcia, Thin Solid Films, 90 (1982), p. 419-423;
and "Chemical Vapor Deposited Copper Indium Diselenide Thin Film Materials
10   Research" Final Report, March 1984, SERI/STR-211-2247. Although these
publications disclose copper indium diselenide/zinc oxide heterojunction formation
using zinc oxide spray pyrolysis or ion beam sputtering respectively, neither method
results in an efficiency of greater than 2-3%. Accordingly, these publications do not
disclose a commercially viable method for the replacement of CdS with zinc oxide in
15   a thin film copper indium diselenide heterojunction cell.

U.S. Pat. No. 4,612,411, describes the preparation of a thin film heterojunction
photovoltaic cell formed from copper indium diselenide, as a first semiconductor
layer, and the formation of a two layer, zinc oxide semiconductor in heterojunction
with the copper indium diselenide. The first of the two zinc oxide layers comprises a
20   relatively thin layer (100-2000 angstroms) of high resistivity zinc oxide and the
second comprises a relatively thick (10,000 angstroms) zinc oxide layer doped to
exhibit low resistivity.

U.S. Pat. No. 5,474,939, produces a higher efficiency non-CdS cell through
the application of a wet chemical deposition zinc hydroxide precipitation step. This
25   process involves the use of a metal back contact having a first p-type semiconductor
film of chemical vapor deposition ("CVD") copper indium diselenide and a second
transparent n-type semiconductor film of CVD zinc oxide on the copper indium
diselenide and a thin interfacial film of transparent insulating zinc oxide, between the

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p-type copper indium diselenide film and the n-type zinc oxide. The interfacial zinc oxide film is prepared by chemical deposition of zinc hydroxide on the copper indium diselenide from a zinc salt solution and complexing agents comprising ammonium hydroxide or triethanolamine, to form a zinc ammonium solution complex, and

5   annealing the deposit to convert the zinc hydroxide into the zinc oxide. While this patent uses a wet chemical deposition step of zinc hydroxide precipitate from solution to generate a thin interfacial zinc oxide layer, the devices prepared by direct deposition of a zinc oxide layer on copper indium diselenide films are only 2-4% conversion efficient in spite of utilizing films capable of producing 15-17% cells.

10   Accordingly, there is a need in the art to obtain copper indium gallium diselenide thin film photovoltaic cells characterized by high conversion efficiency without incurring the disadvantages of: utilzing a CdS layer via wet chemistry; utilizing slow, batch processes; employing the highly toxic material of Cd, which escalates manufacturing costs as a result of handling and disposal of this hazardous

15   waste; incurring a reduction in collected current; and forming junctions at 60-80°C.

Disclosure of the Invention

One object of the present invention is to provide an improved process for making $CuInGaSe_2$ thin film solar cells characterized by conversion efficiencies greater than about 11%, and yet avoid the need to deposit a buffer layer.

20   Another object of the present invention is to provide a process for preparing $CuInGaSe_2$ thin film solar cells characterized by conversion efficiencies greater than about 11% by subjecting $CuInGaSe_2$ thin films to an evaporant species from zinc acetate dihydrate to dope the surface region n-type.

Other objects and advantages of the invention will become apparent from the

25   drawings and detailed description of the preferred embodiment of the invention hereafter described.

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Brief Description of the Drawings

FIG. 1 is a graph showing current density versus voltage for a $CuInGaSe_2$ (CIGS) thin film or diode that was not subjected to an evaporant species of zinc acetate dihydrate and on which ZnO was sputter deposited.

5   FIG. 2 is a graph showing current density versus voltage for a CIGS thin film subjected to an evaporant species of zinc acetate dihydrate at a substrate temperature or Tg of 150°C, followed by sputter depositing ZnO.

FIG. 3 is a graph showing current density versus voltage for a CIGS thin film subjected to an evaporant species of zinc acetate dihydrate at a substrate temperature

10   or Tg of 200°C, followed by sputter depositing ZnO.

FIG. 4 is a graph of current density versus voltage for a CIGS thin film subjected to an evaporant species of zinc acetate dihydrate at a substrate temperature or Tg of 250°C, followed by sputter depositing ZnO.

FIG. 5 is a CIGS film on Mo/glass cut into three 2" x 1" samples (A1, A2 and

15   A3) and a blank, wherein one CIGS sample and a blank is used in each run of the invention process, and the blank is saved as the bottom third.

FIG. 6 is a graph showing dark and light I-V curves for the 7 cells shown on a substrate $1 \times 1.5 in^2$ shown in FIGS. 6A thru 6G. The film were subjected to evaporant species from zinc acetate dehydrate at 150°C, followed by sputter depositon of ZnO.

20   Each figure is for one cell, and the two lines are for dark and light I-V.

FIG. 6H shows a quantum efficiency curve of relative external quantum efficiency (QE) versus wavelength for the ZnO/CIGS cells of FIGS. 6 prepared by the Zn vapor phase doping of the invention process.

FIG. 7A through 7G are graphs showing two sets of I-V curves for a string of

25   seven cells adjacent to each other on a single substrate, one for dark and the other for light, $1 \times 1.5 in^2$. The broken lines are I-V curves taken after the cells are annealed in air at 200°C for 2 minutes. The CIGS absorber was exposed to evaporant zinc acetate   ·
dehydrate at a substrate temperature of 100°C, and heated to 200°C for 30 minutes.

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FIG. 8A through 8F are graphs showing I-V curves of the distribution of efficiency for multiple cells on a single substrate, wherein the CIGS sample was exposed to evaporant species from zinc acetate dehydrate at a substrate temperature of 200°C and the ZnO layer was deposited by sputtering. There are many cells with an

5 efficiency of 11%, and the best cell had an efficiency of 12.6%.

FIG. 9 is a graph showing I-V curves using essentially the same criteria as FIGS. 8A through 8F, but has an efficiency of 13.1%, an open current voltage of 0.627V, a current density of $32.8 mA/cm^2$, and a fill factor of 64%.

Detailed Description of Preferred Embodiment of Invention

10 It is known that Cd and Zn have a profound influence in creating efficient photovoltaic junctions in $CuInSe_2$ (CIS) thin films since 11% cells can be fabricated in CIS thin films with Cd and Zn. On the other hand, with $CuInGaSe_2$ thin films, 15.7% cells have been produced using Cd and 14.2% cells have been produced using Zn. By the use of a non-aqueous method to diffuse Zn a cell with 13.5% efficiency is

15 produced.

With demand mounting in the thin film photovoltaic industry, CIS cells can benefit greatly from a simple, quick, in-line process for doping and junction-formation. The present invention process meets this demand in that hot CIGS is cooled to about 200°C, and made to enter a doping zone wherein it is exposed to an

20 evaporant species of $ZnAc_2 \cdot 2H_2O$ or its equivalents, and exits to the transparent conducting oxide (TCO) deposition of ZnO by sputtering.

Equivalents of zinc acetate dehydrate in the context of the invention process are zinc chloride, zinc iodide, and zinc bromide. Further, cadmium chloride, cadmium iodide, and cadmium bromide will produce effects similar to that of the

25 aforementioned zinc compounds.

In the vapor phase and n-type doping and junction formation of $CuInGaSe_2$ thin film CIGS cells of the invention, the CIGS thin films were subjected to an evaporant species from zinc acetate dihydrate at various substrate temperatures. The

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samples were etched in acetic acid and solar cells were completed by the sputter
deposition of ZnO to obtain cells as high as ~ 11% efficiency for the case of 200°C
and this is a marked improvement compared to the 1.8% efficiency for the case of no-
vapor phase ZnO sputter deposition treatment. As a consequence, a non-Cd, in-line
5   junction fabrication process for CIGS is now available for the photovoltaic industry.

EXAMPLE

A co-evaporated CIGS film was divided into four parts, 2" x 1" in length and
loaded into a chamber along with a Mo/glass substrate. Zinc acetate dihydrate solid
was loaded in a Mo boat. A thermocouple touching the back side of the CIGS
10   substrate was used to control the temperature (Tglass).

The zinc acetate dihydrate source temperature was raised slowly and the
charge was evaporated slowly, while the substrate is brought to the desired
temperature before the evaporation is started. The substrate was exposed during the
entire time. The exposure time was not controlled, and the evaporation lasted for
15   about 2 to about 4 minutes. The samples were removed and etched in 50% acetic acid
to remove the ZnO deposit. Sputtered ZnO was deposited next in MRC.

The graph of FIG. 1 shows a weak diode in the case of no treatment in
accordance with the invention process.

In FIG. 2 where Tg = 150°C, and was treated in accordance with the invention
20   process, the sample had a dark brown coating, and showed deposition of ~30nm ZnO
or $Zn(OH)_2$ film. For Tg = 200°C and 250°C, as shown respectively in the graphs of
FIG. 3 and 4, no clear change in color was observed. All the samples were etched in
acetic acid.

In the case where the Tg=150°C, a clear improvement is observed, and the Jsc
25   is in the expected range. Further, there is > 60% fill factor, and this is an indication
that the process is satisfactory. The Voc is nearly 0.5V, and this is again in the range
for non-CdS cells as > 9% efficiency is obtained.

For Tg = 200°C, the Voc is 0.562V, and the fill factor is 0.63. These are
satisfactory numbers. The typical Voc's for aqueous Cd photoelectric treated cells are

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about 0.6V, and fill factors are about 0.65-0.7. The diode formed functions satisfactorily in darkness and light. A reaction at the surface of the CIGS is raising the potential barrier (spike) and limiting the current flow; however the absorber is likely compensated, as (p is reduced by Zn donors). The cross over is indicative of defects

5   changing occupancy under illumination (trapping).

For Tg = 250°C, as shown in FIG. 4, these problems become worse. The absorber is now semi-insulating due to excessive compensation. There is a similar trend with CdS/CIGS as a function of post heating.

FIG. 5 is a CIGS film on Mo/glass cut into three 2" x 1" samples (A1, A2 and

10   A3) and a blank, wherein one CIGS sample and a blank is used in each run of the invention process, and the blank is saved as the bottom third.

FIG. 6 is a graph showing dark and light I-V curves for the 7 cells shown on a substrate 1x1.5in² shown in FIGS. 6A thru 6G. The film were subjected to evaporant species from zinc acetate dehydrate at 150°C, followed by sputter depositon of ZnO.

15   Each figure is for one cell, and the two lines are for dark and light I-V.

FIG. 6H shows a quantum efficiency curve of relative external quantum efficiency (QE) versus wavelength for the ZnO/CIGS cells of FIGS. 6 prepared by the Zn vapor phase doping of the present invention process.

FIG. 7A through 7G are graphs showing two sets of I-V curves for a string of

20   seven for cells adjacent to each other on a single substrate, one for dark and the other for light, 1x1.5in². The broken lines are I-V curves taken after the cells are annealed in air at 200°C for 2 minutes. The CIGS absorber was exposed to evaporant zinc acetate dehydrate at a substrate temperature of 100°C, and heated to 200°C for 30 minutes. The data for the two sets of curves are shown below:

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Cell	Process	Area (cm²)	Voc (V)	Jsc (mA/cm²)	Isc (mA)	FF (%)	Eff (%)	Vmp (V)	Imp (mA)	Pmax (mW)	Rso (Ω-cm)	Rsho (Ω-cm)
1	As dep	0.430	0.490	-30.32	-13.039	65.61	9.751	0.369	-26.45	9.751	2.718	673.9
2	As dep	0.430	0.487	-29.43	-12.655	65.49	9.385	0.365	-25.72	9.385	2.559	717.5
3	As dep	0.430	0.479	-29.55	-12.708	64.75	9.161	0.359	-25.55	9.161	2.149	523.1
4	As dep	0.430	0.474	-29.90	-12.859	64.67	9.161	0.353	-25.93	9.161	2.752	622.0
5	As dep	0.430	0.465	-30.47	-13.100	65.17	9.230	0.350	-26.35	9.230	1.920	566.5
6	As dep	0.430	0.460	-31.46	-13.529	64.39	9.320	0.345	-27.02	9.320	2.411	562.4
7	As dep	0.430	0.458	-30.85	-13.265	63.61	8.986	0.337	-26.69	8.986	2.044	539.8

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4	As dep	0.430	0.474	-29.90	-12.859	64.67	9.161	0.353	-25.93	9.161	2.752	622.0
5	As dep	0.430	0.465	-30.47	-13.100	65.17	9.230	0.350	-26.35	9.230	1.920	566.5
6	As dep	0.430	0.460	-31.46	-13.529	64.39	9.320	0.345	-27.02	9.320	2.411	562.4
7	As dep	0.430	0.458	-30.85	-13.265	63.61	8.986	0.337	-26.69	8.986	2.044	539.8

1	02m200	0.430	0.513	-29.96	-12.883	67.27	10.349	0.395	-26.20	10.349	2.441	402.6
2	02m200	0.430	0.508	-29.08	-12.504	65.86	9.732	0.383	-25.39	9.732	2.498	507.0
3	02m200	0.430	0.501	-29.20	-12.555	63.24	9.246	0.373	-24.76	9.246	2.717	349.8
4	02m200	0.430	0.496	-29.51	-12.689	60.57	8.856	0.369	-24.02	8.856	2.756	319.5
5	02m200	0.430	0.492	-30.00	-12.902	60.05	8.856	0.363	-24.37	8.856	2.742	271.5
6	02m200	0.430	0.492	-31.06	-13.355	61.61	9.424	0.363	-25.94	9.424	2.582	331.9
7	02m200	0.430	0.491	-30.22	-12.993	62.36	9.255	0.369	-25.11	9.255	2.482	283.4

FIG. 8A through 8F are graphs showing I-V curves of the distribution of efficiency for multiple cells on a single substrate, wherein the CIGS sample was exposed to evaporant species from zinc acetate dehydrate at a substrate temperature of 200°C and the ZnO layer was deposited by sputtering. There are many cells with an efficiency of 11%, and the best cell had an efficiency of 12.6%. The data for these two sets of curves are shown below:

Cell	Process	Area (cm²)	Voc (V)	Jsc (mA/cm²)	Isc (mA)	FF (%)	Eff (%)	Vmp (V)	Imp (mA)	Pmax (mW)	Rso (Ω-cm)	Rsho (Ω-cm)
1	As dep	0.430	0.516	-30.62	-13.166	57.59	9.103	0.404	-22.52	9.103	2.431	71.79
2	As dep	0.430	0.532	-31.34	-13.475	67.76	11.293	0.423	-26.69	11.293	1.962	242.87
3	As dep	0.430	0.516	-30.84	-13.262	50.33	8.005	0.384	-20.85	8.005	2.625	50.65
4	As dep	0.430	0.540	-30.97	-13.316	70.91	11.862	0.433	-27.39	11.862	1.814	805.79
5	As dep	0.430	0.542	-30.04	-12.916	71.08	11.576	0.433	-26.73	11.576	1.703	966.72
6	As dep	0.430	0.548	-30.19	-12.983	71.47	11.818	0.440	-26.84	11.818	1.966	1062.24
7	As dep	0.430	0.563	-30.98	-13.323	72.54	12.647	0.453	-27.91	12.647	1.620	1119.81

FIG. 9 is a graph showing I-V curves using essentially the same criteria as FIGS. 8A through 8F, but has an efficiency of 13.1%, an open current voltage of 0.627V, a current density of 32.8mA/cm², and a fill factor of 64%.

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As a result of these tests, it seems apparent from these cells that several issues are significant:

     1.   It appears useful to characterize the ZnO ($Zn(OH_2)$) deposit by XRD;

     2.   It may be useful to utilize a high efficiency, well characterized absorber;

     3.   It may be useful to use a shutter and control the exposure time;

     4.   It may be useful to evaporate zinc acetate on CIGS that is not heated, and post annealing appears useful to induce diffusion and doping;

     5.   It may be useful to either keep the ZnO on or remove it; and

     6.   It may be useful to wash the CIGS in water or dilute NH_4OH before deposition to remove surface alkali impurities.

That a simple evaporation process of a Zn species, that may be zinc acetate dihydrate for vapor phase, extrinsic n-type doping of CIGS thin films can achieve at least 11% conversion efficiency in CIGS cells is apparent from the J-V data which follows.

Although certain preferred embodiments have been described and shown in the examples and the accompanying drawings, it is to be understood that these embodiments are merely illustrative of and not restricted to the invention scope and various modifications and changes may occur to those of ordinary skill in the art without departing from the spirit and scope of the invention, which is described hereinafter in the affixed claims.